

A review of sample preparation and its influence on pH determination in concrete samples

S. Manso✉, A. Aguado

Polytechnic University of Catalonia – (Barcelona, Spain)
✉sandra.manso@upc.edu

Received 30 September 2015

Accepted 13 May 2016

Available on line 20 January 2017

SUMMARY: If we are to monitor the chemical processes in cementitious materials, then pH assays in the pore solutions of cement pastes, mortars, and concretes are of key importance. However, there is no standard method that regulates the sample-preparation method for pH determination. The state-of-the-art of different methods for pH determination in cementitious materials is presented in this paper and the influence of sample preparation in each case. Moreover, an experimental campaign compares three different techniques for pH determination. Its results contribute to establishing a basic criterion to help researchers select the most suitable method, depending on the purpose of the research. A simple tool is described for selecting the easiest and the most economic pH determination method, depending on the objective; especially for researchers and those with limited experience in this field.

KEYWORDS: pH; Concrete; Mortar; Cement paste; Pore solution.

Citation/Citar como: Manso, S.; Aguado, A. (2017) A review of sample preparation and its influence on pH determination in concrete samples. *Mater. Construcc.* 67 [325], e108. <http://dx.doi.org/10.3989/mc.2017.08515>

RESUMEN: *Revisión sobre la preparación de muestras de hormigón y su influencia sobre la determinación del pH.* Determinar el pH de la fase acuosa de los poros de pastas de cemento, morteros y hormigones tiene gran importancia en el monitoreo de los procesos químicos que tienen lugar en los materiales cementicios. Sin embargo, no existe una normativa que regule el método de preparación de la muestra para la determinación de su pH. Este artículo presenta un estado del conocimiento de diferentes metodologías para la determinación del pH de materiales cementicios y la influencia del método de preparación según el objetivo. Además, se presenta una campaña experimental comparando tres técnicas diferentes. Dicha campaña contribuye a establecer un criterio simple que ayude al investigador en la selección del método más adecuado dependiendo del objeto de estudio. Este artículo tiene por objetivo ser una herramienta sencilla para seleccionar la metodología más fácil y económica para determinar el pH dependiendo del objetivo, especialmente para investigadores noveles o aquellos con escasa experiencia.

PALABRAS CLAVE: pH; Hormigón; Mortero; Pasta de cemento; Solución porosa.

ORCID ID: S. Manso (<http://orcid.org/0000-0002-2712-5976>); A. Aguado (<http://orcid.org/0000-0001-5542-6365>)

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1. INTRODUCTION

The measurement of pH provides relevant information on the status of both living and inert systems. In living systems, pH plays an important role

in various contexts such as within the human body and the soil. For instance, the pH range of the epidermis is between 4 and 6.5. Its protective function prevents dehydration through the skin and functions as a barrier to microorganisms (1). In soils,

pH influences both nutrient uptake and the biomass composition of fungi and bacteria (2). As regards inert systems, the analysis of pH was of significant interest to Van der Schueren and De Clerck (3) in their study of pH-sensitive textiles proposed as wound dressings.

It is likewise of interest in the study of cementitious materials. For example, pH is of interest when studying setting and hardening processes, the use of hydraulic binders in cementitious materials with a low pH, and hydraulic binders as a complement to other tests in the diagnosis of pathologies such as decalcification.

The hydration of cementitious materials involves a sequence of chemical reactions between the solid components of the cement and water (4). The pH range over which CSH gels remain stable is between 10.18 and 12.48 (5). Therefore, pH has a key role in the chemical kinetics of those reactions and provides important information when studying their evolution during setting and hardening processes.

Cementitious materials with a low pH are also used in mixes that contain waste products with both inorganic and organic contaminants. At a high pH, of around 12 and 13, inorganic contaminants are precipitated as insoluble hydroxides, as the minimum solubility of those hydroxides ranges between 8 and 11. However, highly alkaline systems are not suitable for organic contaminants, as the most effective method for fixing them requires the presence of microorganisms, which can grow and survive within a pH range of 5.5 to 8.5 that is required for biodegradation processes (6).

Finally, decalcification of the cement paste is provoked by chemical attacks such as carbonation, leaching, and aggressive sulfates (7). Concrete carbonation is an important cause of deterioration in reinforced concrete structures. It is a process by which atmospheric carbon dioxide reacts with the hydration products of the cement to form calcium carbonate, which lowers the alkalinity of the concrete. Carbonation is therefore responsible for depassivation of the reinforcement steel (8).

Leaching is a process which takes place when concrete is exposed to poorly mineralized or acidic water. The phenomenon consists of the dissolution of calcium and hydroxide ions out of the matrix, which increases its porosity and causes other changes in the material (9–10).

In contrast, sulfate attack refers only to the negative effects of the chemical reactions in which sulphate ions are present (11). However, the attack severity depends on the exposure conditions such as temperature and sulphate concentrations, among others (12).

According to Grubb et al. (13), “pH is an approximate measure of the acidity or the alkalinity of a solution and is defined as the negative logarithm of the hydrogen-ion (H^+) concentration”. The measurement of this parameter in a

cementitious material is therefore a challenge; there is no standard method for pH determination in the pore solutions of concrete samples, nor is there a sample-preparation method for that purpose. As pH can only be measured in liquid mediums, a means of accessing the pore solutions of hardened materials is needed.

Several methods have been proposed in the literature, such as pore pressing, dispersion in distilled water of crushed and ground samples, full immersion of the sample in distilled water, in-situ leaching (ISL) in small sample cavities, etc. However, there are no studies that compare the different preparation procedures, while assessing any influence that they may have on the pH of the pore solution. So, the selection of the method for the pH assay of cementitious materials and its regulation would be useful, as neither a standard sample-preparation method, nor a method to determine the pH of pore solutions exists at present.

A state-of-the-art approach of the aforementioned methods is therefore examined in this paper, in which the pH of hardened cementitious materials is analyzed and each method, its influence on the results, and its advantages and drawbacks are discussed. Furthermore, an experimental program was conducted to compare three of those methods, so as to determine whether the sample preparation procedure influenced the pH assay: full immersion in distilled water, dispersion in distilled water of crushed and ground samples, and superficial measurement by means of flat-surface pH electrodes.

2. METHODOLOGIES

2.1. Indicators

The use of indicators such as phenolphthalein or bromothymol blue has been fully described in the literature. Phenolphthalein has traditionally been used to determine the altered zones of cementitious materials, as it dyes materials with a pH of over 9 in a purple-red color.

Chemical changes involving the use of phenolphthalein to determine the drop in pH mainly refer to carbonation due to environmental CO_2 (14–15) and acid attack (16–17). Figure 1 shows an example of a sample affected by carbonation.

The use of phenolphthalein is an easy and cheap indicator and therefore the most common method for visual determination of carbonation. However, it provides no accurate information on the pH of the material. Several authors have proposed more accurate methods (18–19). For instance, ASTM International (20) suggested the use of thymolphthalein as a good substitute. Thymolphthalein turns from blue to colorless within an approximate pH range of 9.3 to 10.5, while phenolphthalein turns from red-violet to colorless between a pH range of

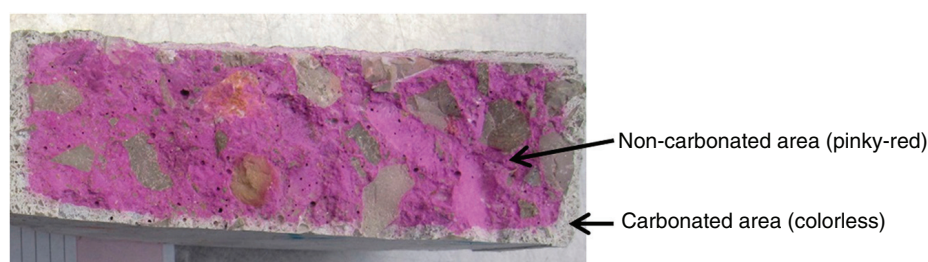


FIGURE 1. Carbonation front determined with phenolphthalein.



FIGURE 2. Alkaline pH values indicators.

8.9 to 9.8. These results can therefore provide useful indications of early carbonation.

Furthermore, it could be of interest to study the process of pH reduction in terms of a combination of indicators. Figure 2 shows four different pH indicators for the alkaline range of pH values, which may be used for that purpose. Other indicators also used for the analysis of particular compounds include the pH indicator bromophenol blue that determines free lime in hydrated cement following titration (21). In addition, Knopf et al. (22) used bromothymol blue which registers lower pH levels than phenolphthalein. This indicator has also been used by other authors such as Guilbeau et al. (23) and in other disciplines such as dentistry (24).

2.2. pH strips

The use of pH indicator strips is extensive in areas such as medicine and biology. For instance, Ericson and Bratthall (25) proposed the use of acid-impregnated pH indicator strips to estimate salivary buffer capacity. Moreover, Islander et al. (26) used the same type of strip to verify pH measurements recorded with flat-surface electrodes. These strips are also common in microbiology for monitoring the pH of culture media (27). Accordingly, Matinlinna et al. (28) determined the pH of different dental silanes with pH indicator strips.

However, the use of this simple technique is less common for cementitious materials. The literature contains few works on their use in building materials; those that do refer mainly to pH verification following accelerated carbonation processes (29–30). Previous work has been based on standard ASTM

F710 (31), which refers to a procedure to determine the pH of concrete floors prior to the resilient flooring applications. According to the aforementioned standard, several drops of distilled water should be placed on a clean surface and the pH assay should be done after 60 ± 5 seconds.

As with pH indicators, the use of pH strips for simple verification of the carbonation state of a concrete sample is both cheap and easy. The method simply involves placing a pH strip in contact with a few drops of distilled or deionized water on a concrete surface. However, this method should only be used for verification of alterations in the state of a material. Grubb et al. (13) suggested that the method could be applied in field tests to concrete powder scratched off concrete surfaces and mixed with 10 to 12 drops of water.

Islander et al. (26) used pH-indicator strips to validate the accuracy of the results from flat-surface electrodes. They opened a slight depression on the surface, to facilitate contact between the drops of distilled water and the electrode and to avoid problems relating to specimen roughness.

2.3. pH-meters

The use of digital equipment yields more accurate results than colour-coded methods. These modern methods are now the most widely employed to estimate the pH of a heterogeneous and mainly solid material such as concrete. Pore-water expression (PWE) is considered the most accurate index and the reference method. Proposed by Longuet et al. (32), it consists of pore-solution extraction under high pressure. An amount of 300 g of cement paste is subjected to a maximum pressure of 350 MPa. However, only certain samples may be used in the proposed equipment and the characteristics of this method means that only the pore solution of cement pastes can be obtained. Therefore, Barneyback and Diamond (4) proposed modifications to the equipment, to permit the extraction of pore solutions from the mortar. To that end, maximum pressures in the order of 550 MPa were applied to 250 g of the sample. Nevertheless, the configuration of the equipment and its constituent parts, which are presented in Figure 3, were similar.

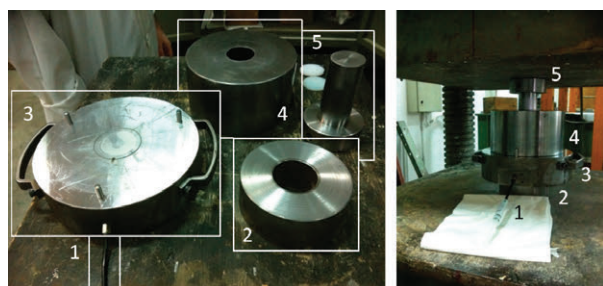


FIGURE 3. Pore-pressing equipment (1. Plastic tube for liquid drain; 2. Support cylinder; 3. Platen; 4. Die Body; 5. Piston assembly).

The literature lists a wide range of pressures applied to cement pastes and mortars to obtain a suitable amount of pore solution for the test procedure. Accordingly, the pressures applied to cement pastes varied between 345 MPa and 560 MPa, although it was not specified by all of the authors (33–36). Similar figures may be observed in the literature on the pressures applied to obtain pore solutions from mortars, which generally ranged between 200 MPa and 1,100 MPa (37–41).

The diversity of the methods leads to a question on the possible effect of the pressure on the results. Constantiner and Diamond (42) evaluated the effects of a range of pressure between 248 MPa and 517 MPa. The authors concluded that slight increments of alkali hydroxide were observed at higher pressures, as well as an increase in sulphate ion concentrations. However, no works on that topic have been found in the subsequent literature.

Traditionally, direct measurement of the pore solution has been considered a reference method. However, the technical and equipment-related costs are high and sufficient samples are not always easy to obtain. Therefore, effort had gone into the development of methods that reduce both costs and difficulty. In this sense, several variations of the ex-situ leaching (ESL) approach have been used. Basically, the aforementioned method corresponds to mixing deionized water and powder from crushing a known weight of material. However, there is an important question regarding the liquid-to-solid (L:S) ratio, the state of the sample (powdered, crushed, or in one piece) and the leaching period, which will all have significant influence on the pH results, due to the effect of dilution.

Regarding the L:S ratio, several authors used a ratio of 1, although other variables differed. For instance, Mori et al. (43) assayed pH after suspending 1 g of mortar in 1 ml of distilled water, while Räsänen and Penttala (44) crushed 30 g of mortar to mix 15 g with 15 ml of distilled water for their assay. Afterwards, the mixture was stirred at 35 rpm for 15 minutes and 10 ml of the total volume was used for the determination of the pH. Wang et al. (45) crushed and ground cement pastes to obtain a

fine powder (sieved with #200 sieve) and diluted it with water. Then, the mixture was shaken for 5 minutes and was finally filtered to determine the pH of the filtrate solution. Similarly, Song et al. (46) mixed 100 g of different cements and 100 ml of distilled water. The mixture was shaken for 1 hour and then filtered, to determine the pH of the filtrate.

In contrast, other authors have used a different L:S ratio and variations of the above methods. Webster and Loehr (47) used an L:S ratio of 20, Ha-Wong et al. (48) used a ratio of 13, Gowripalan and Mohamed (49) referred to an L:S ratio of 2, Paglia et al. (50) determined the pH of a mixture with an L:S ratio of 80, Garrabrants and Kosson (51) and Dinakar et al. (52) used a ratio of 5, and Ottosen and Rørig-Dalgaard (53) used an L:S ratio of 2.5. Nevertheless, the most widely used ratio was 10, once again varying the procedures that were followed prior to measurement (54–58).

Pavlik (59) analyzed pore solutions with the ESL method testing the effect of all three variables: particle size of the sample (0/0.5, 0.5/1 and 1/2 mm, L:S ratio (1, 2, 5 and 50) and leaching time (up to 24 hours). The author concluded that the effect of particle size for maximum sizes of 2 mm will be low if a low L:S ratio is used. Moreover, he recommended a maximum L:S ratio of 5 for cement pastes, without any specific recommendations for leaching time.

Regarding the state of the sample, the results between powdered and non-powdered samples may differ significantly, which is also linked to the L:S ratio. As Li et al. (38) previously pointed out, the hydration of anhydrous particles will occur when cementitious material samples are ground to powder, specially when using high L:S ratios. Li et al. (38) studied the effect of the L:S ratio and the leaching period of powdered samples, comparing four different L:S ratios (0.7, 1, 2 and 4) and four leaching periods (1, 3, 10 and 30 days). The authors concluded that the optimum leaching period for the samples under analysis would be a minimum of 3 days, depending on the alkalinity of the material. Moreover, an L:S ratio of 1 was suggested to avoid or to minimize the hydration of anhydrous particles.

Nevertheless, the concern regarding the dilution effect was first expressed by Sagües et al. (60). The authors stated that the pH of the leachate was less than the real pH of the pore solution and difficulties on developing a correction were analyzed. Therefore, the ISL method was proposed as an alternative. In that method, small holes of approximately 5 mm diameter and 25 mm deep are drilled into the saturated specimens' surface and 1 ml of distilled water is placed in the holes. Then, an acrylic washer and a rubber stopper prevents carbonation and permits the pH to be measured over time. Figure 4 shows a 3D scheme with all the components.

However, variations of the ISL method such as the ex-situ leaching method have been used.

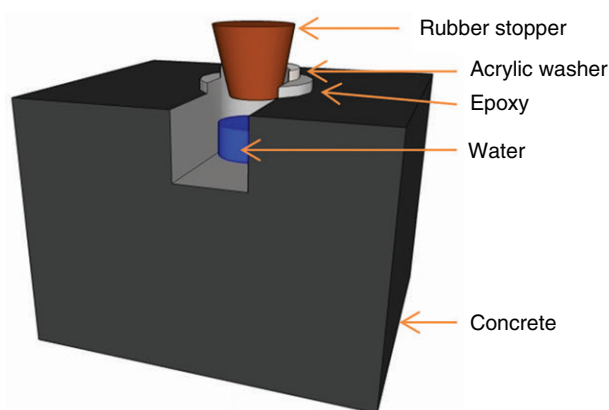


FIGURE 4. 3D scheme of the ISL method proposed by Sagües et al. (60).

Li et al. (38) proposed holes of 3 mm in diameter and 30 mm deep filled with 0.2 ml of distilled water. Later, Caseres et al. (61) produced holes of 3.6 mm diameter and 35 mm deep, filling them with 0.22 ml.

Up to this point, PWE, ESL and ISL have been identified as the main procedures for the analysis of pore solutions. When using those methods, other chemical analyses are performed as the purpose is usually more than a simple estimation of pH. Therefore, when the pH is the only parameter of interest, several authors have suggested the use of flat-surface electrodes. The basic procedure consists of pouring a drop of distilled water on a clean surface of the specimen and immediately placing the electrode in contact with the water. The main problem that remains is the sensitivity of the glass electrode and the danger of scratching in contact with the rough material. Islander et al. (26) proposed this method to measure the pH of corroded concrete. Later on, Ehrich et al. (62), Robert et al. (63) and Okabe et al. (64) all used it to study the alterations to cementitious materials produced by microorganisms.

Similarly, Heng and Murata (65) proposed a method in which a 6 mm diameter filter paper is placed on the clean surface and 100 μ l of distilled water is poured onto it. Then, a waiting time of 15 minutes is necessary, adding more distilled water if necessary so that the filter paper will not dry out. Afterwards, a flat-surface electrode is placed on the filter paper for the pH measurement. Rostami et al. (66–67) and Shao et al. (68) followed exactly the same procedure, except for the size of the filter-papers (10 x 10 mm²).

Comparisons between methods for a better understanding of their results have prompted multiple publications. Li et al. (38) compared the PWE against the ISL method and concluded that the ISL method provided a representative estimation of pH in agreement with PWE tests. Similarly, Björk and Eriksson (54) compared the PWE with

the ESL method and detected the dilution effect, obtaining lower pH values when using the ESL method. Räsänen and Penttala (43) used titration with phenolphthalein of the extracted pore solution to validate the results obtained from the ESL method. Additionally, the authors suggested the powder portion used in the ESL method should range between 40% and 60% of the total weight of the mixture.

After comparing both the PWE and the ISL methods, Li et al. (40) compared the PWE and the ESL methods. The applied pressure was significantly lower (200 MPa) compared to their previous work (650 MPa) and the authors focused the ESL method on comparing four different L:S ratios and four different leaching periods. In terms of the different methods, the ESL method with an L:S ratio of 1 and a leaching time of 3 days related best to the PWE result.

Grubb et al. (13) studied the influence of the amount of sample, dilution ratio, waiting time and temperature and compared three different procedures for pH assays. The authors reported that aspects such as waiting time and sample amount, while the dilution ratio is maintained, had non-significant influence on the results. However, parameters such as solution temperature and dilution ratio may influence the resultant pH. Furthermore, the authors compared the use of pH indicator strips according to standard ASTM F710 (31) and the use of a pH-meter on concrete sample powder in dilution. The results showed significant differences, with pH values ranging from 10 to 12.

3. EXPERIMENTAL PROGRAM

An experimental program was performed to compare two different methods over 28 days. The selected methods were ESL with samples in powder and non-powder form, and the flat-surface electrode method proposed by Heng and Murata (65).

Cement pastes and mortar specimens were produced with Ordinary Portland Cement type I 52.5R and distilled water with a water to cement ratio (w/c) of 0.5. Silica sand was used in the production of the mortar specimens, according to standard UNE-EN 196-1:2005 (69) (a:c:w = 3:1:0.5). A total of 24 cement-paste samples each weighing 15 g and 12 mortar specimens measuring 40 x 40 x 160 mm³ were produced.

Three cement-paste samples and three mortar specimens were individually immersed in distilled water with an L:S ratio of 10. As a non-destructive method, pH was measured at the different testing ages. Three other cement pastes and three mortar specimens per testing age were crushed and ground to powder until the material passed a #100 sieve. Then, 10 g of each sample were added to 100 ml of distilled water and vigorously shaken for 5 minutes.

The pH assay was performed after one hour, under stirring. Finally, the other three cement-paste samples and three mortar specimens were used for pH assay with a flat-surface electrode. A drop of distilled water was poured on the surface of the specimen and the electrode was then positioned in place. Three different points were fixed on each face of the specimen, in order to monitor pH evolution of the same parts with the same specimens for all testing ages.

Figure 5 shows the results obtained for cement-paste samples and mortar specimens following the three aforementioned methods over 28 days. The results pointed to a closer similarity of pH results after 1 day than after 28 days, especially when following the results from the flat-surface electrode. Evolution of pH using the ESL method showed a fast increase over the first three days before reaching equilibrium. In contrast, the flat-surface electrode (FSE) method that measured the wet filter paper in contact with the surface of the specimen failed to provide valid results. The standard deviation obtained for the two variations with the ESL method was lower than 0.05 while for the FSE it was up to 0.9. Moreover, the recorded drop in pH may be a consequence of local dissolution of the superficial Portlandite (70) and should be considered a methodological error.

Comparing the curves, slight differences were obtained between the two variations of the ESL method, which were observed over the first 3 and 5 days for cement pastes and mortars, respectively. The different pH readings corresponded to the different times the solutions needed to reach equilibrium. The higher specific surface of the powdered particles in relation to the specific surface of the non-powdered specimens meant that equilibrium was reached earlier in the powder suspension, even though the L:S ratio was the same. Moreover, that fact is also a consequence of the lower amount of

hardened cement paste in the cases of the mortar samples.

The results obtained for the FSE method showed similar values to those of the ESL method for the first 3 days and for the first 1 day, for the cement pastes and the mortars respectively. However, the evolution over time showed a drop in pH, as previously suggested, due mainly to the dissolution of the portlandite. The results presented above support the fact that proper planning and selection of the right method should always be done.

4. SELECTION CRITERIA

In this section, an analysis of the main advantages and drawbacks of the different methodologies will be presented. According to the above results as well as the experimental program, it is important to consider that all those methods are valid, although differences in terms of ease of testing, urgency of results, cost, accuracy, and monitoring evolution over time have been detected between them. Six different methods were analyzed: pH indicators, pH-indicator strips, PWE, ESL, ISL and FSE.

Accuracy should not be a requirement when the purpose of the test is to determine the state of the material. Usually, pH indicators such as phenolphthalein are spread onto a cross-section of the specimen, so as to detect the carbonation depth. In this sense, indicators will provide a binary response: i.e. purple dye on non-carbonated areas and colorless dye on carbonated areas.

The results with pH-indicator strips may give a more specific range of pH values. Several ranges of pH values are covered by the industry from the whole pH range to limited ranges of less than 2 points of pH. However, the method is based on comparing the colors of a color-coded strip against a color chart, which means that it is, for example, less accurate than using a pH-meter. Strips are also

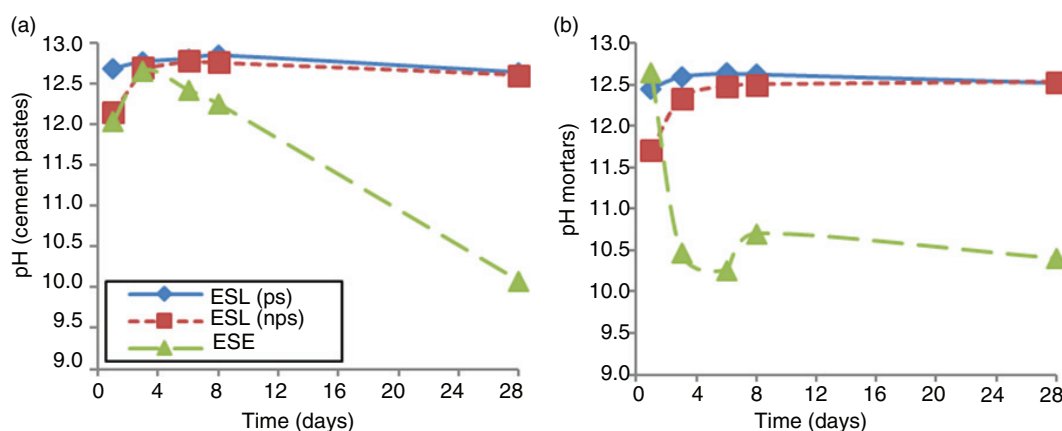


FIGURE 5. pH evolution of cement-paste samples (a) and mortar specimens (b) by means of ex-situ leaching of powdered samples (ESL (ps)), ex-situ leaching with non-powdered samples (ESL (nps)) and the use of a flat-surface electrode (FSE).

a good alternative when the purpose of the study is to determine pH readings on an approximate basis.

The last four methods are considered the most accurate, as the readings are obtained with a pH-meter. However, there are significant differences between their advantages and drawbacks. PWE, ESL and ISL are the most suitable methodologies especially when the purpose of the study is not only pH determination of the pore solution. PWE is the most expensive method due to the equipment and requires previous sample saturation to obtain a large enough volume of the sample. Moreover, the volume of pore solution is low or null depending on the cementitious material. For instance, experiments to try to obtain the pore solution of Ordinary Portland Cement and Magnesium Phosphate Cement mortars by means of this technique were done in previous works (58). However, no pore solution was obtained from any of the Magnesium Phosphate Solution samples and the analysis was not carried out.

The main drawback of the ESL methods consists of the dilution effect due to the L:S ratio leading to an underestimated pH reading. On the other hand, the hydration of anhydrous particles may produce overestimated readings. Therefore, it is really important to calibrate the method in case of using different materials than those previously studied. Nevertheless, as the experimental program has shown, although lower L:S ratios and sufficient leaching time should be applied, further tests comparing a wide range of significant parameters should also be performed. As was also evident from the experimental program, the leaching time should

be determined depending on the specific surface of the sample.

Considering the analysis, Table 1 suggests a tool to select the most suitable method depending on the purpose and considering several factors: how easy is the test, the urgency of obtaining the results, the test budget, and the accuracy of the results, as well as the possibility of studying changes in the pH over time. The different methods were scored on a 1-to-5 scale with 1 as the least suitable and as 5 the most suitable reading. However, the fact that laboratory facilities may change the scores should also be considered. Therefore, the interpretation should be performed considering the lack of specific equipment. The values given in Table 1 correspond to the scores obtained with the following instructions.

The survey of 5 questions called *Ease of testing* collected the yes/no answers and each question received a particular score. A total of 0 points were added for each affirmative response and 1 point was subtracted for each negative answer. The questions are presented below:

- Does the process require more equipment than a pH meter?
- Does the process take more than 5 minutes?
- Does the method require any specific induction without considering calibration and the use of a pH meter?
- In case of requiring the use of a pH meter, is it necessary to use any special electrodes?
- Has the humidity content of the sample or specimen, prior to testing, affected the results?

TABLE 1. pH measurement selection tool

Purpose	Criteria	Methodologies						
		pH indicators	pH strips	PWE	ESL (ps)	ESL (nps)	ISL	FSE
Altered state of the material	Ease of testing	5	5					3
	Urgency of results	5	5					4
	Economic reasons	4	5					3
	Evolution in time	4 ^a	5 ^b					3 ^b
Complete chemical analysis	Ease of testing			1	3	4	2	
	Urgency of results			1	2	3	1	
	Economic reasons			1	2	5	2	
	Result accuracy			5	2	3	4	
	Evolution in time				4 ^a	5	5	
Determining superficial pH	Ease of testing	5	5	1	3	4	2	3
	Urgency of results	5	5	1	2	3	1	4
	Economic reasons	4	5	1	2	5	2	3
	Result accuracy	1	2	5	3	3	4	5
	Evolution in time	2	3	1	1	4	5	3

Range 1 to 5 being 1 the less suitable methodology and 5 the most suitable one. a: Different piece of the specimen should be used; b: Different area of the specimen should be tested; no super index: No special considerations.

The scores associated with the factor *Urgency of results* were established on the basis of the time needed by someone completing the test for the first time. Therefore, the methods requiring more than 1 hour 30 minutes were scored with 1 point; between 1 hour and 1 hour 30 minutes with 2 points; between 30 minutes and 1 hour with 3 points; between 15 and 30 minutes with 4 points; and, less than 15 minutes with 5 points. Those times were defined by previous research in which the same methods were used. However, they may vary depending on the person determining the pH value and the times should be considered as relative.

In contrast, the *Economic reasons* factor was scored according to commercial prices of materials and equipment of comparable characteristics. Scores from 1 to 5 were given, ranging from the most expensive to the cheapest.

Result accuracy scores were based on the results in the literature that has been reviewed in this paper. From the aforementioned analysis, the reference test was taken as PWE, which scored 5 points. Then, other measurements were based on a dilution factor, in which the order of magnitude depended on the selected method. For instance, ESL (ps) might overestimate the pH value due to the hydration of anhydrous cement particles. Moreover, there was a dilution effect of the solid when using the ESL in comparison with the ISL method (60).

Finally, the scores for the factor '*Evolution over time*' corresponded to the sum of the scores given in answer to the following questions (positive responses 0 points and negative responses 1 point):

- Is it necessary to test a different piece of the sample or specimen?
- Is it necessary to test a different measurement area of the sample or specimen when it is possible to use the same piece?
- Should the time between measurements be longer than 1 hour?
- Is it acceptable to obtain results that are not highly accurate? (The concept of "highly accurate" is related to the scores given to points 4 and 5 in the 'Results accuracy' section)
- Is it acceptable to use more equipment than a pH meter?

5. CONCLUSIONS

The pH of cementitious materials provides relevant information on the different chemical processes of cementitious materials. However, the selection of the method is frequently seen as a controversial step in research, especially for scientists new to the topic. Consequently, a review of the different methods is essential before a selection tool may be definitively proposed.

Six different methods have been reviewed: use of indicators, use of pH strips, pore water expression (PWE), ex-situ leaching (ESL), in-situ leaching (ISL) and the use of a flat surface electrode (FSE). The first two are mainly used to determine the state of the material while the other four provide accurate results.

PWE is the reference method due to its high accuracy, although it requires the use of specific equipment. Moreover, the costs related to both the equipment and the technique, promoted the development of the ESL method and the ISL method afterwards. According to the literature, the ESL method overestimates the pH value due to the L:S ratio. Hence, the proposal of the ISL method as an alternative. Finally, the FSE method was proposed to measure the surface pH value. All three - the ESL, the ISL, and the FSE methods - have been contrasted to verify the accuracy of their results. However, more in-depth research comparing all the methods for different purposes might provide a better overall picture.

In conclusion, the criteria proposed here aim to facilitate the selection of the most suitable method. The selection process is accomplished by a tool which scores the different methods depending on the purpose and considering factors such as ease of testing, urgency of results, test budget, accuracy of results, and the possibility of studying changes in the pH over time.

ACKNOWLEDGMENTS

The authors of this paper wish to acknowledge the economic support received from the Spanish Ministry of Economy and Competitiveness through Research Project BIA2010-17478.

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